THE INFLUENCE OF pH-DEPENDENT CATION-EXCHANGE CAPACITY UPON THE LIME REQUIREMENT OF SELECTED KANSAS SOILS

by

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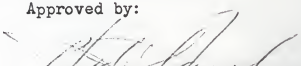
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INTRODUCTION

Cation-exchange capacity (CEC) is known to be influenced by the pH at which it is measured. The purpose of this investigation was to determine the general extent of this influence and the correlation of pH-dependent CEC with the lime requirement of selected Kansas soils.

Currently, little attempt is made in routine soil analysis to adjust either the soil pH to a uniform level before determining CEC or to determine CEC at the pH of the soil by adjusting the pH of the saturating solution. For the purposes CEC data are now being used, the present techniques are probably sufficiently accurate. However, the need may arise where the utilization of more uniform and accurate methods will be required. Strictly speaking, accuracy is lost when the CEC of a given soil is reported without noting the pH at which it was measured. Furthermore, the CEC should be measured at the natural pH of the soil if one is to describe CEC as it naturally exists.

Samples representative of Kansas soils were available for analysis. These soils had been used by Vodraska (33) in evaluating lime requirement testing procedures for use in Kansas. As a result of Vodraska's study, lime requirement testing procedures used by the Kansas Soil Testing Lab were altered. Since Pratt (23) and Helling (11) had reported a direct relationship between lime requirement and pH-dependent CEC, it was thought that a study directed toward pH-dependent CEC would complement work done by Vodraska and would add to the knowledge of the subject.

REVIEW OF LITERATURE

The phenomenon of cation exchange, though unknown by that term has been observed far back in recorded history. However, it was not until the mid-eighteen hundreds that Thompson (15) and Way (15) began serious investigations into this soil characteristic.

By the late 1880's Van Bemmelen (15) had developed the colloidal theory and was using the terms "absorption exchange" and "absorption compounds". Weigner (15) concluded that cation exchange was an adsorptive rather than a chemical reaction.

It was not until 1932 that Mattson and Hester (16) reported that the CEC of the soil was a function of pH. This observation marked the beginning for the work done in this area today.

One cannot fully appreciate the significance of the problem without first understanding the techniques and procedures involved in obtaining CEC data. Thus, a short section will be devoted to CEC determinations.

The basic procedure for determining CEC involves saturating the exchange complex with an index cation, removing excess saturating salt, extracting the index cation, and determining the amount of index cation in the extractant. The amount of index cation in the extractant is equated with the CEC of the soil.

The above description of a procedure for measuring CEC appears to be straightforward and simple. This is not the true situation, however. First, the soil should be at a known pH because it has been shown that CEC is influenced by the pH at

which it is measured. Thus, it is necessary to develop a saturating solution which contains the index cation and is buffered at the pH of the soil or some other reference pH. Furthermore, the index cation which is chosen should effect good cation replacement, be easily extracted, and its concentration in the extractant readily determined.

The buffered $BaCl_2$-triethanolamine solution developed by Mehlich (18) and modified by Pratt (23) appeared to have these desirable characteristics. These solutions were well buffered at high pH values, gave excellent cation replacement, were adaptable to soils containing carbonates, and barium is readily determined by flame emission techniques.

Mehlich (19) noted that the use of the $BaCl_2$-triethanolamine solution occasionally gave low CEC results. Helling (11) found the triethanolamine (TEA), which was used to increase the buffering capacity at high pH values, often behaved as a cation in acid solutions. This was especially noticeable in soils containing clay minerals of the 2:1 lattice type. Adsorption of the TEA instead of the index cation would give low CEC values since CEC is equated with the concentration of the index cation in the extractant.

To avoid this problem, Helling developed a buffered saturating solution using monochloroacetic acid instead of TEA. This solution was strongly buffered at low pH values whereas the solutions used by Mehlich and Pratt were more strongly buffered at high pH values. The choice of the pH of the buffered saturating solution should be dependent upon the purpose for which

the CEC data are to be used.

The choice of index cation has been considered to be a factor of importance in measuring CEC. Index cations which have been used with varying degrees of success are sodium (4), barium (10, 18, 19, 20, 22, 23, 24), calcium (12, 13), potassium (25, 32), and ammonium (5, 14, 31).

Differences in the measured CEC also results from using different index cations. This variability of results has been attributed largely to differences in susceptibility of the index cations to hydrolyze during the washing step. As excess saturating salt is washed from the soil sample, some index cations will be lost from the exchange complex by hydrolysis and some excess salt will be retained. Hydrolysis errors which occur during the washing step were reported by Chapman and Kelley (5) in 1930, and examined more closely by Bower et al. (4) in 1952. Okazaki et al. (21) re-emphasized recently that a balance of these errors is rarely achieved. Thus, the magnitude of the error is uncertain. Okazaki et al. (22) found that no significant differences attributable to the use of barium or sodium as the index cation could be noted when the procedure did not include a washing step. Bower et al. (4) and Okazaki et al. (22) found that hydrolysis errors did not generally exceed 4% of the CEC.

One generally accepted procedure for determining the amount of washing necessary to remove excess saturating salt is by anion analysis. Where the anion is chloride, the soil sample is washed until the final washing gives a negative silver nitrate test for

chloride. Occasionally, a soil will disperse before the washing is complete and completing the washing step becomes a problem.

Another error, pointed out by Baker (1), results from contamination of the leachate by the ethanol in the washing solution. Baker reported that a small amount of ethanol in the leachate will result in large positive errors during the analysis for the index cation by flame emission procedures. This error can be eliminated by heating the soil sample in a hot-water bath until the ethanol has been driven out of the soil sample.

Barium is readily determined using the Beckman DU flame photometer. However, the determination can be made with greater speed and accuracy using the atomic absorption spectrophotometer.

Coleman et al. (6), Pratt (23), and Helling et al. (11) separated CEC into two basic components. These two components have been referred to as the permanent charge and pH-dependent CEC or the low and high pH components. Coleman pointed out that this separation may be more complicated than first impressions would suggest. The permanent charge, low pH component, was considered to be the sum of the metallic cations and hydrogen which were exchangeable with a neutral salt solution such as a N potassium chloride solution (11, 23). Although it is convenient to speak of CEC as containing high and low pH components, it should be recognized that the CEC of many soils continuously increases with increased pH (11, 23).

Two reports are cited here to illustrate that the separation of CEC into permanent and pH-dependent fractions is not always a precise separation. It was postulated by Schofield and Sampson

(29) in work done on soil kaolins that the lack of increase in CEC from pH 2 to 6 was due to internal compensation of charge. Schofield (28) reports similar findings on latosols. The results of these reports were interpreted as meaning that permanent charge does not have the same significance in these soils as with pure three-layer clays.

Pratt (23) found that a high correlation exists between lime requirement and pH-dependent CEC. Pratt defined pH-dependent CEC as the difference in CEC measured at pH 8.0 and the CEC measured at the pH of a 1:5 soil-N KCl suspension. Also, Pratt reported a high correlation between pH-dependent CEC and pH-dependent acidity. The latter characteristic was defined as being the difference in acidity extracted at pH 8.2 and acidity extracted by a N KCl solution.

From Pratt's study it was concluded that the overall reaction of $CaCO_3$ with an acid soil results in an increase in CEC. Pratt summarized the probable reaction as follows:

> (a) an increase in pH of the soil solution caused by the hydrolysis of $CaCO_3$, (b) dissociation of H^+ ions from pH-dependent ion-exchange sites, and (c) the simultaneous adsorption of Ca^{++} ions on the sites from which H^+ ions dissociated, formation of H_2CO_3 and decomposition of H_2CO_3 to produce H_2O and CO_2. Since neutral salts do not displace the pH-dependent acidity, it is assumed that the Ca^{++} from $CaCO_3$ can be adsorbed on these sites only after the H^+ ions have dissociated as a result of increased pH.

The role of aluminum in permanent and pH-dependent CEC has been explored by several investigators. McLean et al. (17) interpreted results obtained on Ohio soils as meaning that exchange sites on organic matter which were occupied by aluminum

were responsible for the increase in CEC with increased pH. Bhumba and McLean (2), again on Ohio soils, reported that CEC measured with unbuffered salt solutions markedly increased with liming soils high in soluble aluminum. Volk and Jackson (34) have similarly mentioned the presence of aluminum as contributing to pH-dependent CEC of Wisconsin soils.

Vodraska (33) found that extractable aluminum in acid Kansas soils was not the main factor which influenced the variability of results obtained using different lime requirement testing procedures.

MATERIALS AND METHODS

Experimental Equipment

All weight measurements were made with a Sartorius single pan balance to the nearest milligram. A Fisher Accumet pH meter with glass electrode was used to measure pH. An International Centrifuge No. 1 was used for reclaiming soil from suspension. Analysis for barium was made on a Perkin-Elmer atomic absorption spectrophotometer, model 303. Samples were shaken using a Burrell Wrist-Action shaker.

Experimental Procedure

Collection and Preparation of Soil Samples. The soil samples used had been obtained by Vodraska (33) for use in evaluating lime requirement testing procedures through the co-operation of County Agents over the state of Kansas. The soil samples submitted were selected from acid and unlimed soils. The samples were collected from the surface soil in the same manner as for general fertility tests. The samples were air-dried at room temperature, ground to pass through a 40 mesh sieve, and thoroughly mixed prior to analysis.

Selection of samples to be included in this study were made on the basis of results obtained by Vodraska. Soils were selected so as to give a wide range of the following soil characteristics:

1. lime requirement
2. natural pH in the acid range
3. extractable aluminum content

Cation-Exchange Capacity Determination.

I. Reagents

Buffered Saturating Solution - The procedure outlined by Helling (11) was used in preparing the buffered saturating solution. Barium was the index cation used in this saturating solution. A one normal hydrochloric acid solution was used to adjust the pH of two equal portions of the stock buffered saturating solution to pH levels of 2.50 and 3.50. Equal portions of the remaining stock buffered saturating solution were adjusted to pH levels of 5.00, 6.00, 7.00, and 8.00 with a saturated barium hydroxide solution.

II. Procedure - The following modification of the Helling (11) method was used:

1. Approximately 4 g of air-dry soil were weighed out to the nearest milligram in a 100 ml, round-bottom centrifuge tube. A separate soil sample was taken at this time for moisture content determination.
2. A 50 ml aliquot of the buffered saturating solution at the appropriate pH was added to the centrifuge tube, the tube stoppered, and the samples shaken for from 10 to 12 hours.
3. The suspension was then centrifuged at RCF = 1.956×10^6 for five minutes and the supernatant liquid discarded after determining its pH.
4. Steps two and three were repeated until no change was noted in the pH of the supernatant buffer

solution. At this point it was assumed that the pH of the soil was at the pH of the supernatant buffer solution. Only three or four periods were required to bring the soils to pH values of from 2.50 to 7.00. The soils required five or six shaking periods to bring the soils to a pH of 8.00 due to the low buffering capacity of the solution at this pH.

5. Then, 50 ml of 0.5 N $BaCl_2$ solution, containing 5 ml of buffered saturating solution at the appropriate pH, was placed in the centrifuge tube and the soil was re-suspended. This step was included to insure complete saturation of the exchange complex with barium. This step may not be required in all cases because saturation is probably complete at the end of step four. Re-runs of several samples on which this step had been omitted revealed no significant change in the measured CEC.
6. Excess barium and chloride ions were removed by repeated washings of the soil sample with absolute methanol. The methanol was removed by centrifuging the samples at RCF = 1.956×10^6 for five minutes and decanting the supernatant liquid. Removal of excess barium and chloride was assumed to be complete when the final washing did not indicate the presence of chloride when tested with silver nitrate. Several soils dispersed before removal of

excess salt was complete. In these cases, the samples were centrifuged for an additional 30 minutes to clarify the suspension.

7. Excess methanol was removed by heating the soil sample in a hot-water bath.
8. Adsorbed barium was removed from the exchange complex by extraction with neutral N ammonium acetate. This extracting solution was chosen over others for several reasons. Ammonium acetate exhibits little tendency to hydrolyze because it is a neutral salt of a weak acid and a weak base. Also, ammonium acetate tends to lower surface tension so that particle surfaces are well wetted. Furthermore, ammonium acetate is a good replacer of hydrogen and barium ions (10, 24).
9. Barium concentration in the extractant was determined on the Perkin-Elmer atomic absorption spectrophotometer.

Total and Partial pH-Dependent Cation-Exchange Capacity. The lower limit of the pH-dependent CEC was considered to be the CEC measured at the pH of a 1:5 soil-N KCl suspension. CEC at this pH was obtained from the pH versus CEC curve plotted for that particular soil. The upper limit of the partial pH-dependent CEC was arbitrarily set at pH 7.00 and the upper limit of the total pH-dependent CEC was considered to be the CEC measured at pH 8.00.

Total Acidity. The original method proposed by Mehlich (18)

and modified by Pratt (23) was modified for this investigation. The modified method used is as follows:

I. Reagents - The $BaCl_2$-triethanolamine ($BaCl_2$-TEA) extracting solution and mixed indicator, brom cresol and methyl red, were prepared as proposed by Mehlich (18).

II. Procedure

1. Approximately 5 g of air-dry soil were weighed to the nearest milligram, placed in a 100 ml round-bottom centrifuge tube, and 33 ml of $BaCl_2$-TEA extracting solution added. The tube was stoppered and then shaken for from 10 to 12 hours.
2. The suspension was centrifuged at RCF = 1.956×10^6 for five minutes, and the supernatant liquid decanted and saved in a 100 ml volumetric flask. This process was repeated two additional times and the solution made up to volume with $BaCl_2$-TEA solution.
3. Three drops of mixed indicator were added to each of 20 ml aliquots taken from the extracted solution and the aliquots were titrated with standard hydrochloric acid to a faint green end-point. The average value from these three titrations was subtracted from a blank titration and the results converted to milliequivalents of acidity per 100 g of soil.

KCl-Exchangeable Acidity. The procedure as proposed by

Helling (11) was used for the determination of KCl exchange acidity. The procedure involves extraction of a soil sample with neutral N KCl and titration of the extractant with standard NaOH to a phenolphthalein end point. The value obtained is subtracted from a blank titration and converted to milliequivalents per 100 g of soil.

pH-Dependent Acidity. The pH-dependent acidity was considered to be the difference between total acidity and KCl exchange acidity.

Lime Requirement. The lime requirements of the soils investigated were determined by a Vodraska (33) modification of the Shoemaker-McLean-Pratt (30) buffer method. The lime requirement is related to the depression of pH as caused by a soil suspended in a buffer solution.

Particle Size Distribution. The percent sand, silt, and clay was determined by the Buoyoucos hydrometer method (3).

Organic Matter Content. Organic matter content was determined by the Kansas Soil Testing Lab using the colorimetric chromic acid procedure as described by Graham (8).

RESULTS AND DISCUSSION

The analytical data obtained in this study of 21 acid Kansas soils are reported in Tables 4, 5, and 6. Table 4 shows data which relates lime requirement, pH-dependent cation-exchange capacity (CEC), pH-dependent acidity, KCl exchange acidity, and natural pH. Table 5 contains particle size distribution, textural class, and percent organic matter data which further defines the soils used in this investigation. Table 6 contains CEC measurements at six pH levels for the Kansas soils used in this investigation and CEC measured at five pH levels for three clay standards.

Influence of pH upon Cation-Exchange Capacity

It can be observed from the pH versus CEC curves contained in the appendix that, in general, the curves show an increasing slope with increasing pH. Furthermore, the curves are fairly linear in the lower range of pH values.

CEC values were averaged for each pH level at which the determinations were made and the results are shown in Fig. 1. It may be noted from Fig. 1 that the increase in CEC was nearly linear between pH 2.5 and 6 and that the rate of increase through this pH range was 1.7 meq/100 g of soil per pH unit. From pH 6 to 7 and from pH 7 to 8 the rates of increase in CEC averaged 2.1 and 3.8 meq/100 g of soil per pH unit, respectively.

The range of pH-dependent CEC values obtained in this study was not nearly as wide as those obtained by Pratt (23). The pH-

dependent CEC of the Kansas soils ranged from 21.1 to 34.5% of the CEC measured at pH 8. Pratt reported finding a range of 28.1 to 74.6% of the total CEC on California soils.

A possible explanation of the higher and wider range of results obtained by Pratt as compared to those obtained on the Kansas soils lies in the organic matter content of the soils tested. The mean value for the organic matter content found in the California soils was 7.1% with a range of from 1.2 to 26.0%. The mean organic matter content found in the Kansas soils tested was 2.4% with a range of from 1.2 to 4.1%. It will be demonstrated later that the major change in CEC with change in pH can be attributed to the organic matter rather than the clay fraction

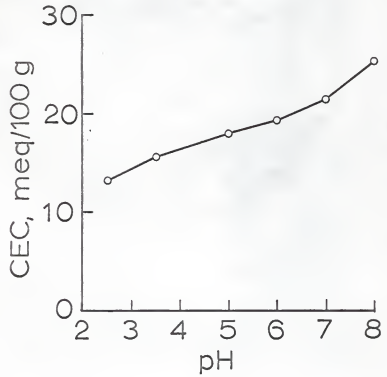


Fig. 1. The average cation-exchange capacity (CEC) values for 21 acid Kansas soils at six pH levels.

of the soil. Thus, the higher and wider range of organic matter contents found in the California soils should cause a higher and wider range of pH-dependent CEC values to be measured in those soils.

Correlation of Total pH-Dependent Cation-Exchange Capacity with pH-Dependent Acidity

Pratt (23) reported a high correlation between pH-dependent CEC and pH-dependent acidity. The pH-dependent CEC was defined in Pratt's study and this study as being the difference in CEC measured at pH 8.0 and the CEC measured at the pH of a 1:5 soil-N KCl suspension. The pH-dependent acidity was defined as the difference in acidity extracted with a salt solution buffered at pH 8.0 and the acidity extracted with N KCl unbuffered solution.

The simple linear correlation coefficient between total pH-dependent CEC and pH-dependent acidity was found to be 0.994 which is significant at the 1% level. These data are shown graphically in Fig. 2.

The results are in agreement with the work reported by Pratt. This high correlation strongly suggests that the increase in CEC with associated increase in pH is due to the opening of exchange sites occupied by H^+ ions. This assumption has validity since the slope of the regression line is nearly 1:1 and the correlation between pH-dependent CEC and pH-dependent acidity is 0.994.

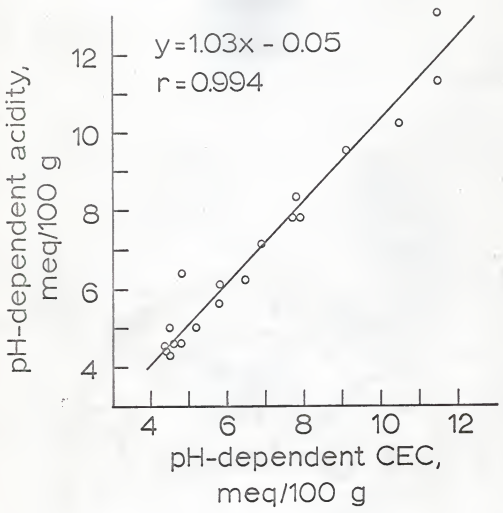


Fig. 2. The regression between the soil pH-dependent cation-exchange capacity (CEC) and the soil pH-dependent acidity for 20 acid Kansas soils.

Correlation of the Lime Requirement with Total and Partial pH-Dependent Cation-Exchange Capacity

The total hydrogen ions in the soil solution of an acre furrow slice at any one time can be neutralized by less than a pound of calcium carbonate. Consequently, most of the lime added to an acid soil is used to neutralize both the KCl-exchangeable and the pH-dependent acidity held on the clay and organic matter surfaces. An examination of the data in Table 4 shows that virtually all of the lime requirement for the 20

soils would be utilized in neutralizing the pH-dependent rather than the KCl-exchangeable acidity. Soil number 8458 from Bourbon County contained the maximum KCl-exchangeable acidity encountered in any of the soils, both on a relative and on an absolute basis. Yet the KCl-exchangeable acidity in soil number 8458 accounts for less than 4% of the lime requirement of this soil. Thus, one would expect a high correlation between lime requirement and pH-dependent acidity or pH-dependent CEC in the 21 Kansas soils. Results obtained by Pratt (23) on California soils add support to this expectation.

Since soils are normally limed to a pH of 7, the "partial pH-dependent CEC", i.e., the difference in the CEC measured at pH 7.0 and the CEC measured at the pH of a 1:5 soil-N KCl suspension, was used to determine if the partial pH-dependent CEC was a better estimator of soil lime requirement than was the total pH-dependent CEC.

Results shown in Table 1 indicate a higher correlation between lime requirement and partial pH-dependent CEC than between lime requirement and total pH-dependent CEC. However, both correlations were significant at the 1% level. These relationships are further illustrated by Fig. 3.

It should be noted that Table 1, column b, contains the correlation coefficients obtained when the Cherokee County soils' data were deleted from the statistical analysis. Later in the discussion, correlations obtained without data from the Cherokee County soils will be referred to this section for comparison.

Table 1. Linear correlation coefficients between lime requirement and either partial or total pH-dependent CEC for 20 Kansas soils (a), and with Cherokee County soils deleted (b).

Test	Correlation coefficient, r	
	(a)	(b)
Lime requirement and partial pH-dependent CEC	0.947**	0.936**
Lime requirement and total pH-dependent CEC	0.845**	0.812**

**Significant at the 1% level.

If the hypothesis is true that pH-dependent cation exchange sites are activated by raising the soil pH due to lime additions, then these correlations are to be expected. Since the lime requirement tests estimate the amount of $CaCO_3$ required to raise the soil pH to 7.0, it is reasonable to assume that the reaction of the $CaCO_3$ would be with pH-dependent cation exchange sites activated below pH 7.0. Thus, the higher correlation between lime requirement and the partial pH-dependent CEC as compared to the correlation between lime requirement and total pH-dependent CEC, shown in Table 1, seems logical.

Based on this data, it was concluded that the partial pH-dependent CEC is an accurate measure of the "true" lime requirement of the soil. Because the KCl-exchangeable acidity was less than 4% of the total pH-dependent acidity, it was also concluded that liming an acid soil increases the CEC of the soils by an amount nearly equal to the lime requirement expressed as milliequivalents per 100 grams. It would be interesting to compare

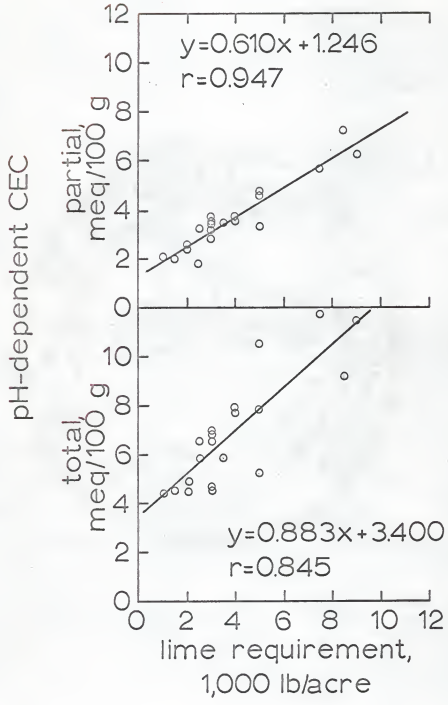


Fig. 3. The regression of lime requirement upon either partial or total pH-dependent CEC for 20 Kansas soils.

the availability or activity of calcium adsorbed on pH-dependent cation exchange sites.

The correlations between lime requirement and either total or partial pH-dependent CEC (Table 1) were not as high as the correlations between pH-dependent CEC and pH-dependent acidity (Fig. 3). The reason for this difference is offered as being due to the relative accuracy of the measurements involved. The testing procedure used for determining the lime requirement by the SMP method was not considered to be as accurate as those used to determine either pH-dependent acidity or pH-dependent CEC. Lime requirement was measured by a single pH measurement whereas pH-dependent acidity was measured by titration and pH-dependent CEC was based on the quantitative determination of barium using the atomic absorption spectrophotometer.

The SMP method has been evaluated for use on Kansas soils by Vodraska (33) and was found to be highly correlated, $r = 0.91$, with the lime requirement as measured by $Ca(OH)_2$ titration to pH 7.0.

Multiple Regression Analysis of the Influence of Extractable Aluminum and Either Partial or Total pH-Dependent Cation-Exchange Capacity upon Lime Requirement

Several investigators (2, 7, 17, 34) have reported that aluminum influences soil acidity. Vodraska (33) correlated extractable aluminum with lime requirement as estimated by the Woodruff (35) and the Shoemaker-McLean-Pratt (SMP) (30) buffer methods and by $Ca(OH)_2$ titration. The correlation coefficients

obtained were 0.65, 0.69, and 0.69, respectively. Thus, it was concluded that the presence of aluminum did not explain the variability of lime requirements as estimated by these methods.

Since extractable aluminum data were available from Vodraska's study, it was convenient and of interest to determine if the inclusion of extractable aluminum with total or partial pH-dependent cation-exchange capacity would increase the correlation with lime requirement.

It should be pointed out that the data obtained from the Cherokee County soils were not included in this section of statistical analysis. Routine checking of the natural pH and lime requirements of the soils revealed values differing from those reported by Vodraska for the Cherokee County soil samples. Thus, to eliminate the possibility of erroneous correlations, these data were deleted.

For the purposes of comparing correlations obtained in this section with those reported in Table 1, column b of Table 1 contains correlations which were obtained between lime requirement and either partial or total pH-dependent CEC without the data from the Cherokee County soils.

Based on extractable aluminum, partial or total pH-dependent CEC, and the SMP lime requirement, multiple regression equations were constructed to estimate lime requirement. The multiple regression correlation coefficients, R, illustrating the predictability of lime requirement based on extractable aluminum and either partial or total pH-dependent CEC, are shown in Table 2. The results are presented graphically in Figs. 4 and 5. The

following relationships were found:

$$Y = 1.460\ X_1 - 0.129\ X_a - 1.257 \quad (1)$$

$$Y = 0.599\ X_2 + 2.053\ X_a - 1.369 \quad (2)$$

where, Y = predicted lime requirement, meq $CaCO_3$/100 g

X_1 = partial pH-dependent CEC, meq/100 g

X_2 = total pH-dependent CEC, meq/100 g

X_a = extractable aluminum, meq/100 g

Table 2. Multiple regression correlation coefficients illustrating the predictability of lime requirement based on the regression relating lime requirement with extractable aluminum and either partial or total pH-dependent CEC.

Test	Multiple correlation coefficient, R
Lime requirement versus extractable aluminum and partial pH-dependent CEC	0.936**
Lime requirement versus extractable aluminum and total pH-dependent CEC	0.912**

**Significant at the 1% level.

Comparison of equations 1 and 2 reveals that the influence of pH-dependent CEC in predicting lime requirement decreases slightly when total is substituted for partial pH-dependent CEC. It may be noted that this substitution resulted in a decrease of from 1.460 to 0.599 meq $CaCO_3$ per meq of pH-dependent CEC. Based on the mean total and partial pH-dependent CEC values for the 17 Kansas soils, this was a decrease in estimated lime requirement contributed by pH-dependent CEC from 5.7 to 4.3 meq

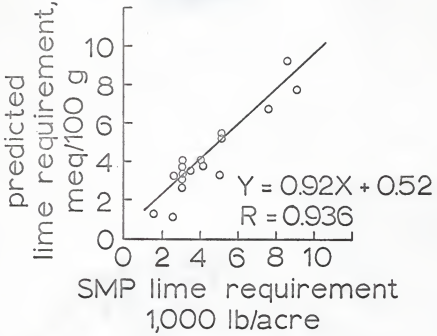


Fig. 4. Scatter diagram illustrating the predictability of lime requirement based on the regression equation relating Shoemaker-McLean-Pratt (SMP) lime requirement to partial pH-dependent CEC and extractable aluminum in 17 Kansas soils.

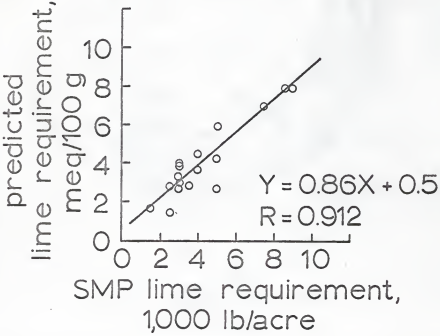


Fig. 5. Scatter diagram illustrating the predictability of lime requirement based on the regression equation relating Shoemaker-McLean-Pratt (SMP) lime requirement to total pH-dependent CEC and extractable aluminum in 17 Kansas soils.

$CaCO_3$/100 g of soil. This trend suggests that the increase in CEC from pH 7 to 8 does not influence the estimation of lime requirement as much as the pH-dependent CEC below pH 7. This observation tends to support the conclusions drawn from the data presented in Table 1 when partial and total pH-dependent CEC were compared for predicting lime requirement.

Directing attention toward extractable aluminum in equations 1 and 2 when total was substituted for partial pH-dependend CEC, another trend may be observed. It may be noted that the contribution of extractable aluminum increased from -0.129 to 2.053 meq $CaCO_3$ per meq of extractable aluminum. Since the mean extractable aluminum content of the soils tested was 0.65 meq/100 g of soil, this increase was from -0.08 to 1.33 meq $CaCO_3$/100 g of soil. This increase was considerably larger than was noted for the pH-dependent CEC. Comparison of Tables 1 and 2 reveals that when extractable aluminum was included with total pH-dependent CEC in the regression equation the correlation between predicted and actual lime requirement was improved.

This section may be summarized by comparing the correlation coefficients presented in Tables 1 and 2. This comparison reveals that the partial pH-dependent CEC alone was as adequate for predicting lime requirement as was partial pH-dependent CEC plus extractable aluminum. Furthermore, the use of partial pH-dependent CEC was slightly better than either total pH-dependent CEC alone or total pH-dependent CEC plus extractable aluminum for the estimating of lime requirement.

Influence of Clay and Organic Matter upon Cation-Exchange Capacity at Six pH Levels

Results obtained by Helling (11) indicated that the CEC of a soil within a given region can be predicted with a high degree of accuracy based on the clay and organic matter content of the soil. Helling pointed out that the use of regression equations constructed for this purpose are limited to a specific geographical and climatic zone. Within this area the clay and organic matter fractions are assumed to be essentially homogenous from one soil sample to another and vary only in the amounts of the components present.

Data obtained on 19 Kansas soils were used to construct multiple regression equations for the purpose of estimating CEC at six levels of pH. These equations along with their multiple correlation coefficients are presented in Table 3. Figure 6 graphically illustrates the results obtained using these regression equations.

The influence of pH upon the CEC of the clay and organic matter can readily be noted by observing the regression equations. Neglecting the regression constants, it can be noted that the CEC contributed by the clay increases from only 0.607 to 0.848 meq/g of clay in the pH range of from 2.5 to 8. These values are comparable with those obtained by Helling (11) which were 0.38 and 0.64, respectively, on Wisconsin soils. Thus, the increase in CEC induced by raising the pH from 2.5 to 8 was by a factor of 1.69 on the Wisconsin soils and 1.40 on the Kansas soils. This difference is understandable since the clay

minerals present are likely to vary from the Wisconsin soils to the Kansas soils.

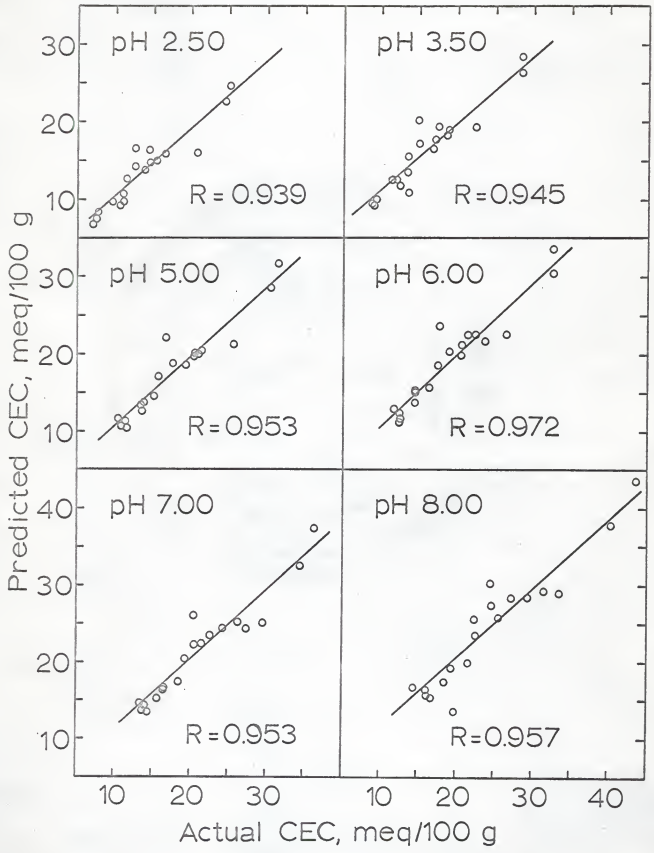
Table 3. Multiple regression data for 19 Kansas soils relating cation-exchange capacity (Y) at six pH levels with percent clay (X_1) and percent organic matter (X_2).

pH	Correlation coefficient, R	Regression equation	
2.50	0.939**	$Y = 0.607X_1 + 0.729X_2 - 3.655$	(3)
3.50	0.945**	$Y = 0.644X_1 + 0.735X_2 - 2.104$	(4)
5.00	0.953**	$Y = 0.680X_1 + 1.413X_2 - 2.496$	(5)
6.00	0.971**	$Y = 0.709X_1 + 1.398X_2 - 1.849$	(6)
7.00	0.953**	$Y = 0.716X_1 + 2.068X_2 - 1.388$	(7)
8.00	0.957**	$Y = 0.848X_1 + 2.516X_2 - 2.413$	(8)

**Significant at the 1% level.

The increase in CEC of the organic matter is considerably higher than for the clay through the same pH range. CEC of the organic matter increased from 0.729 to 2.516 meq/g of organic matter from pH 2.5 to 8. Thus, the CEC of the organic matter at pH 8 was found to be 3.46 times greater than the CEC at pH 2.5, on the average. This increase was contrasted with a 5.92 increase factor reported by Helling. The factor by which organic matter was multiplied in the regression equations constructed by Helling increased from 0.62 at pH 2.5 to 3.66 at pH 8. Since the mean organic matter content of the Wisconsin soils was 3.2% with a range of from 0.51 to 6.5%, it is likely that the

Fig. 6. Scatter diagrams showing the predictability of CEC at 6 pH-levels based on the regression equations relating CEC with organic matter and clay.



regression equations constructed by Helling are weighted more heavily toward organic matter content than are the equations constructed from Kansas soil data. The mean organic matter content of the Kansas soils was 2.4% with a range of from 1.2 to 4.1%.

Another interesting similarity is noticed between the regression equations constructed by Helling and those of this study. The CEC of the organic matter remained fairly stable from pH 5 to 6 in both studies. Regression equations found in Table 3 show that the CEC of the organic matter averaged 1.41 and 1.40 meq/g at pH 5 and 6, respectively. Helling reported values of 1.27 and 1.30 for the same pH levels. This pH region may represent a CEC buffer zone and may be an interesting area to explore further.

Influence of pH upon Cation-Exchange Capacity of Pure Clay Standards

Clay standards which were used to assess the influence of pH upon CEC in this study and their origin are as follows:

(a) Montmorillonite No. 20 (bentonite); Husband Mine; Polkville, Mississippi.

(b) Kaolinite No. 5; McNamee Pit; Bath, South Carolina.

(c) Illite No. 35; Fithian, Illinois.

The results are reported in Table 6 and graphically illustrated in Figs. 7, 8, and 9.

Russell (27) presented data which showed the CEC of a montmorillonite clay as being 95 meq/100 g in the pH range of from 2.5 to 6, but increased to 100 meq/100 g at pH 7. Pratt (23)

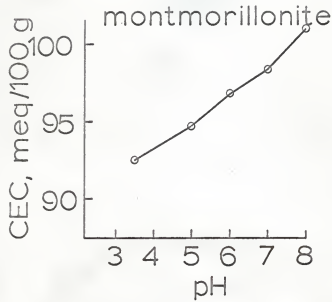


Fig. 7. The influence of pH upon the CEC of montmorillonite as measured at 5 pH levels.

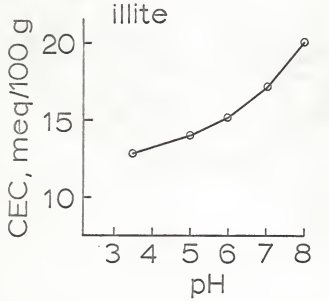


Fig. 8. The influence of pH upon the CEC of illite as measured at 5 pH levels.

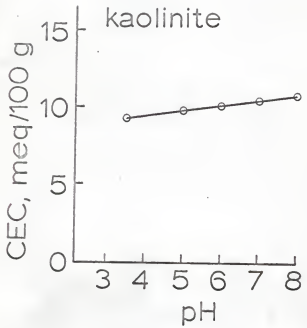


Fig. 9. The influence of pH upon the CEC of kaolinite as measured at 5 pH levels.

reported finding the CEC of a montmorillonite clay to be 96.8, 102.2, and 104.4 meq/100 g at pH 3, 7, and 8, respectively.

Results obtained on montmorillonite in the present study were comparable with those reported by Russell and Pratt. The CEC measured at pH values of 3.5, 7, and 8 were found to be 92.5, 98.4, and 101.0, respectively. These values are somewhat lower than those reported by Pratt but the shape of the curves was comparable. Source of the clay standards used in the various studies could account for the small differences in the CEC measured.

With respect to illite and kaolinite, review of the literature did not provide data for which results obtained in this study could be compared. However, Grim (9) has estimated that the CEC of illite and kaolinite as being in the range of from 20 to 40 and 3 to 15 meq/100 g, respectively. Results obtained in this study were in general agreement with those values reported by Grim.

It was found that the influence of pH upon the CEC of kaolinite was similar to that observed for montmorillonite. The increase in CEC with increase in pH was distributed equally throughout the pH range so that the resulting curve (Fig. 9) was nearly linear, but considerably less in magnitude than montmorillonite. The increase in CEC from pH 3.5 to 8 was found to be from 9.27 to 10.80 meq/100 g.

It may be noted from Fig. 8 that the influence of pH upon the CEC of illite produced a curve with a slightly increasing slope with increased pH. It may be noted that the increase in

CEC from pH 3.5 to 8 was from 9.3 to 10.8 meq/100 g. On an absolute basis, this increase was not as large as the increase noted for kaolinite but nearly as large as the increase noted for montmorillonite. The increase in CEC, expressed as a percentage of the CEC measured at pH 8, was 35.6 for illite while montmorillonite and kaolinite gave values of only 8.5 and 14.1, respectively.

CONCLUSIONS

It should be recognized that only a small portion of Kansas soils was represented in this study. The conclusions which can be made with respect to the soils tested can be summarized as follows:

1. It appears that Kansas soils do not exhibit such wide ranges of pH-dependent cation-exchange capacity values as reported by Pratt for California soils. The pH-dependent cation-exchange capacity of the Kansas soils tested ranged from 21.1 to 34.5% of the cation-exchange capacity measured at pH 8.0 while a range of from 28.1 to 74.6% was reported in California soils. The low and narrow range of organic matter contents found in the Kansas soils was assumed to be the primary cause for the limited range of pH-dependent cation-exchange capacity values obtained.
2. The influence of pH upon the cation-exchange capacity of the Kansas soils was shown to result in a nearly linear increase in cation-exchange capacity with associated increase in pH. On the average, cation-exchange capacity increased at the rates of 1.7, 2.1, and 3.8 meq/100 g per pH unit through the pH ranges of from 2.5 to 6, 6 to 7, and 7 to 8, respectively.
3. It was concluded that the partial pH-dependent cation-exchange capacity alone was as adequate as partial pH-dependent cation-exchange capacity plus extractable

aluminum in the estimating of lime requirement. Furthermore, partial pH-dependent cation-exchange capacity was slightly better than either total pH-dependent cation-exchange capacity alone or total pH-dependent cation-exchange capacity plus extractable aluminum for the estimating of lime requirement.

4. The use of multiple regression equations for the estimating of cation-exchange capacity shows as much promise for use on Kansas soils as is reported for Wisconsin soils. This conclusion was based on regression correlation coefficients which ranged from 0.939 to 0.971 between predicted and measured cation-exchange capacity at 6 pH levels.

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APPENDIX

Table 4. Data illustrating the relationships among lime requirement, partial and total pH-dependent cation-exchange capacity (CEC), pH-dependent acidity, and KCl-exchangeable acidity.

County	Sample number	pH 1:1 soil-water suspension	pH 1:5 soil-N KCl suspension	Lime requirement, 1,000 lb/acre	pH-dependent CEC, meq/100 g		pH-dependent acidity, meq/100 g	KCl-exchange acidity, meq/100 g
					partial	total		
Barton	16	6.0	5.2	2.5	3.2	6.5	6.1	0.04
Bourbon	8414	5.5	4.6	3.0	3.5	4.6	4.6	0.11
	8457	5.4	4.4	8.5	7.2	9.1	9.5	0.35
	8458	5.5	4.7	7.5	5.6	11.5	13.0	0.10
Chautauqua	4	5.7	5.1	3.0	3.1	6.5	6.2	0.04
Cherokee	2	6.2	5.5	2.0	2.4	4.4	4.4	0.04
	3	6.0	5.3	2.0	2.5	4.8	4.6	0.05
	4	6.6	6.1	1.0	2.0	4.4	4.5	0.03
Coffey	1	5.6	4.6	3.0	3.4	6.8	6.4	0.09
	2	5.5	4.6	5.0	3.3	5.2	5.0	0.08
Edwards	3	6.0	5.3	2.5	1.8	5.8	5.6	0.05
	9	6.2	5.3	1.5	1.9	4.5	4.3	0.01
Jefferson	1	6.2	5.2	4.0	3.7	7.7	8.0	0.06
	B	6.0	5.0	4.0	3.6	7.9	7.8	0.07

Table 4, concluded.

County	Sample number	pH 1:1 soil-water suspension	pH 1:5 soil-N KCl suspension	Lime requirement, 1,000 lb/acre	pH-dependent CEC, meq/100 g		pH-dependent acidity, meq/100 g	KCl-exchange acidity, meq/100 g
					partial	total		
Marshall	3	5.5	4.2	9.0	6.2	11.5	11.3	0.14
	10	5.6	4.6	5.0	4.7	10.5	10.2	0.21
Neosho[1]	4	5.4		12.0				
Saline	5	6.0	5.0	3.0	2.8	4.5	5.0	0.04
	3048	5.9	5.0	3.0	3.5	6.9	7.1	0.06
	3067	5.7	4.8	3.5	3.4	5.8	6.1	0.17
Sumner	440	5.8	4.6	5.0	4.7	7.8	8.3	0.12

[1]Analysis was not completed due to lack of soil sample.

Table 5. Particle size distribution, textural class and organic matter content data which further defines the soils under investigation.

County	Sample number	Particle size distribution			Textural class	Organic matter
		Sand %	Silt %	Clay %		%
Barton	16	28.26	50.16	21.58	Sil	1.6
Bourbon	8414	36.71	45.83	17.46	l	1.7
	8457	13.65	59.12	27.23	Sil	3.0
	8458	9.95	48.10	41.95	SiC	4.1
Chautauqua[1]	4					2.7
Cherokee	2	27.70	56.61	15.69	Sil	2.1
	3	25.70	59.60	14.70	Sil	2.2
	4	26.78	58.54	14.68	Sil	2.0
Coffey	1	12.60	67.00	20.40	Sil	1.4
	2	11.74	60.78	27.48	SiCl	2.5
Edwards	3	22.80	51.60	25.60	Sil	2.6
	9	37.92	42.52	19.56	l	1.2
Jefferson	1	11.01	59.67	29.32	SiCl	2.6
	B	14.90	54.39	30.71	SiCl	2.6
Marshall	3	20.72	50.37	28.91	Cl	2.8
	10	9.17	49.92	40.91	SiC	2.2
Neosho[1]	4					3.0
Saline	5	23.08	49.88	27.04	Cl	2.0
	3048	26.57	48.89	24.54	l	2.0
	3067	35.33	44.71	19.96	l	1.8
Sumner	440	18.84	40.65	30.51	SiC	1.9

[1]Mechanical analysis was not conducted due to lack of soil sample.

Table 6. Cation-exchange capacity (CEC) values measured at 6 levels of pH on 21 selected Kansas soils and 3 clay standards.

County	Sample number	CEC, meq/100 g					
		pH					
		2.42	3.43	4.97	5.98	7.00	8.08
Barton	16	10.86	13.15	15.02	16.38	18.45	21.92
Bourbon	8414	6.62	8.50	10.04	11.71	13.27	14.42
	8457	14.88	18.40	21.13	23.74	27.17	29.32
	8458	24.83	28.06	31.20	32.94	36.22	44.28
Chautauqua	4	12.68	14.39	17.99	19.89	21.17	24.77
Cherokee	2	7.14	9.09	11.16	12.25	13.97	16.13
	3	6.67	8.65	10.75	12.18	13.71	16.13
	4	6.85	8.73	11.24	12.13	14.20	17.02
Coffey	1	10.96	11.80	13.20	14.62	16.28	19.87
	2	14.34	16.92	20.06	20.80	22.66	24.73
Edwards	3	13.56	16.77	19.10	20.48	21.37	25.63
	9	10.51	12.08	13.40	14.42	15.62	18.42
Jefferson	1	20.76	22.32	25.68	26.31	29.61	33.92
	B	12.17	14.75	16.59	17.79	20.15	24.87
Marshall	3	16.28	18.64	21.01	22.44	26.11	31.72
	10	24.08	28.03	30.11	32.80	34.28	40.38
Neosho	4	18.21	20.75	23.58	24.74	27.82	36.65
Saline	5	12.36	14.89	17.16	18.96	20.50	22.27
	3048	10.93	13.09	15.65	17.30	19.14	22.69
	3067	9.29	11.42	13.61	14.43	16.65	19.43
Sumner	440	14.21	17.47	19.99	21.31	24.07	27.48

Table 6, concluded.

Clay standard	Sample number	CEC, meq/100 g				
		pH				
		3.50	5.00	6.00	7.00	8.00
montmorillonite	20	92.46	94.67	96.77	98.41	101.04
illite	35	12.87	14.00	15.14	17.01	20.00
kaolinite	5	9.27	9.89	10.06	10.49	10.80

Fig. 10. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Barton County 16 and Bourbon County 8414.

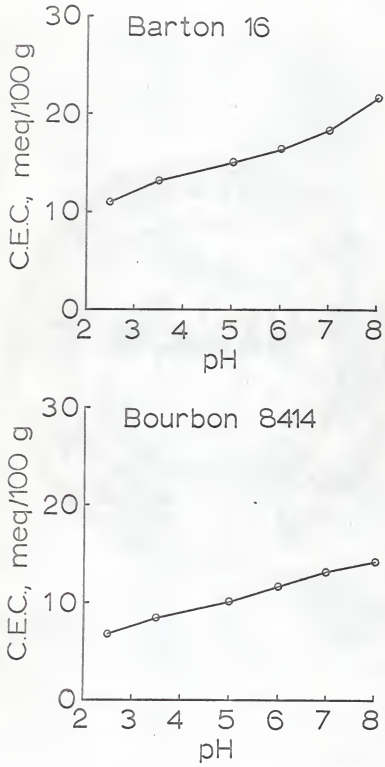


Fig. 11. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Bourbon County 8457 and Bourbon County 8458.

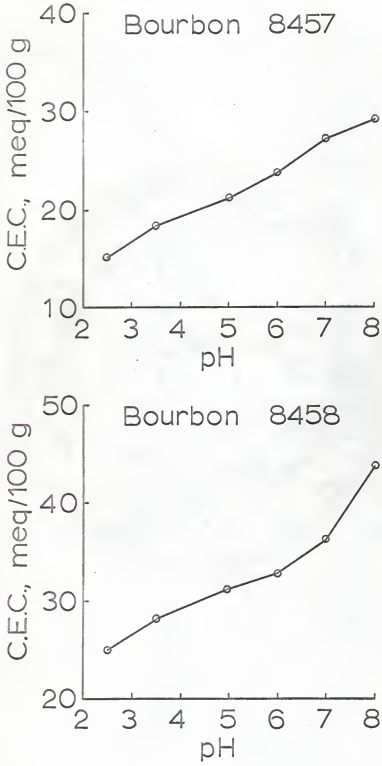


Fig. 12. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Chautauqua County 4 and Cherokee County 2.

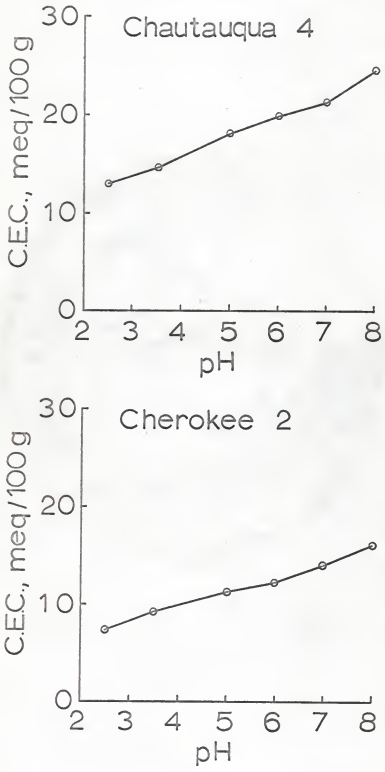


Fig. 13. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Cherokee County 3 and Cherokee County 4.

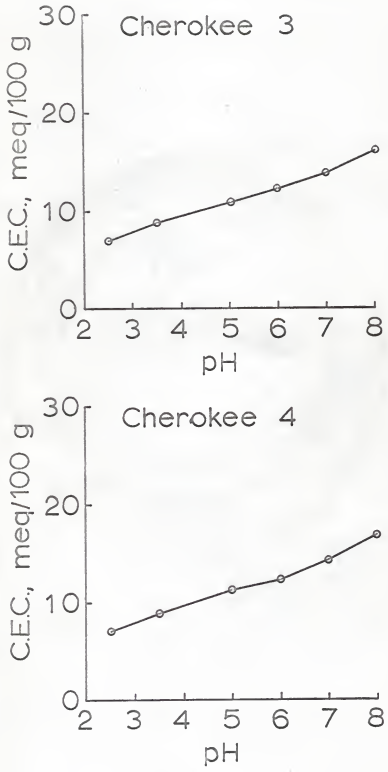


Fig. 14. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Coffey County 1 and Coffey County 2.

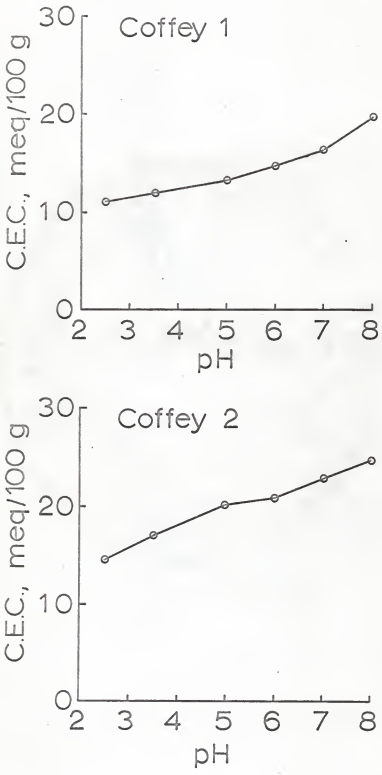


Fig. 15. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Edwards County 3 and Edwards County 9.

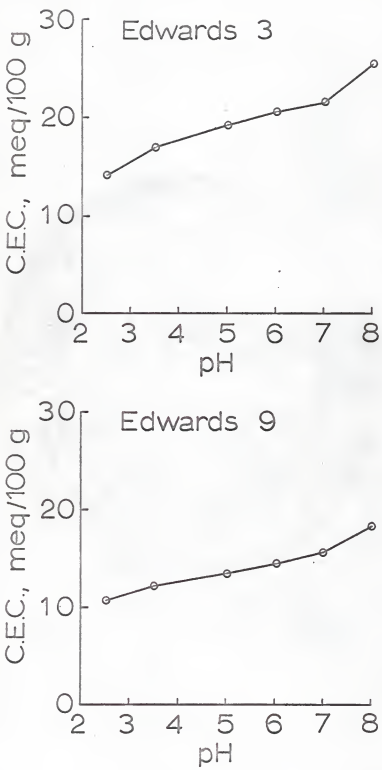


Fig. 16. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Jefferson County 1 and Jefferson County B.

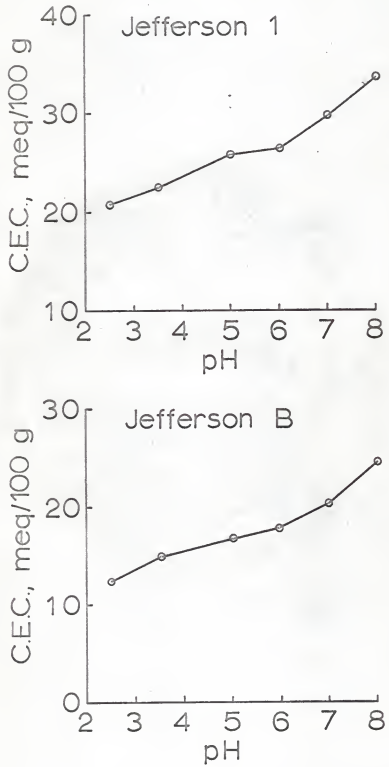


Fig. 17. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Marshall County 3 and Marshall County 10.

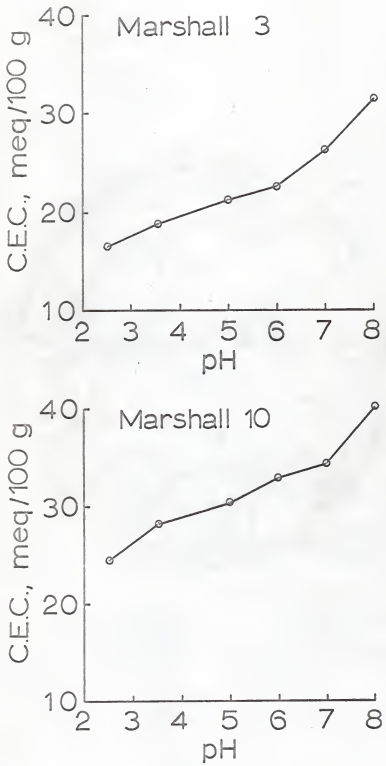


Fig. 18. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Neosho County 4 and Saline County 5.

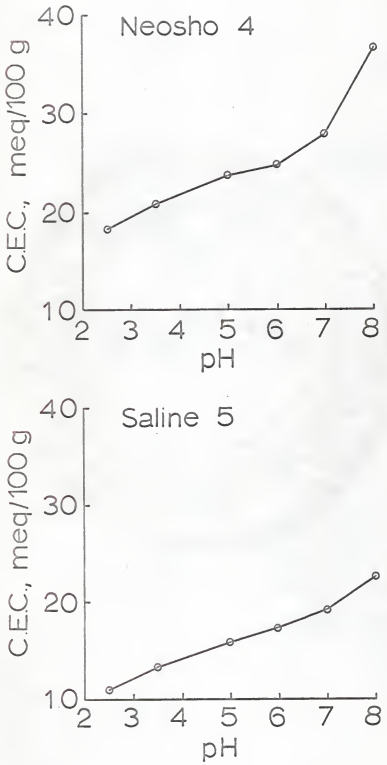


Fig. 19. Curves illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil samples Saline County 3048 and Saline County 3067.

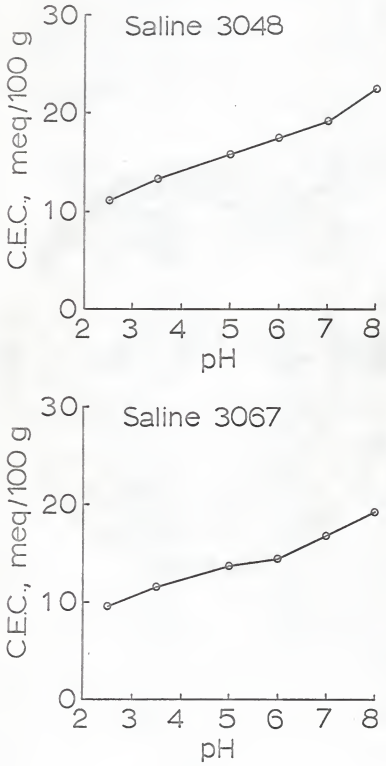
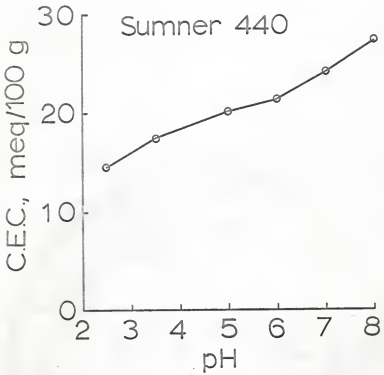


Fig. 20. Curve illustrating the influence of pH upon the cation-exchange capacity (CEC) of the soil sample Sumner County 440.



THE INFLUENCE OF pH-DEPENDENT CATION-EXCHANGE CAPACITY UPON THE LIME REQUIREMENT OF SELECTED KANSAS SOILS

by

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The need for a study of pH-dependent cation-exchange capacity (CEC) as it exists in Kansas soils arose from the fact that: (a) currently there is little attempt to determine CEC at a uniform reference pH and (b) a recent study by Vodraska resulted in a change in the lime requirement testing procedure used in Kansas. Since it had been reported that pH influences measured CEC and pH-dependent CEC was correlated with lime requirement, it was thought that a study directed toward pH-dependent CEC and its relationship to lime requirement would supplement Vodraska's work and add to the knowledge of the subject.

CEC, as influenced by pH, extractable aluminum, clay, and organic matter, was one focal point in this investigation of 21 selected Kansas soils. Also, attention was directed toward the relationships among pH-dependent CEC (partial and total), pH-dependent acidity, and lime requirement.

CEC was determined at 6 pH levels from 2.5 to 8.0, and divided into three parts: permanent charge, partial pH-dependent CEC, and total pH-dependent CEC. The permanent charge, although not measured, was considered to be the sum of those cations exchangeable with a neutral N KCl solution. The lower limit of pH-dependent CEC was considered to be at the pH of a 1:5 soil-N KCl suspension. The upper limit of the partial pH-dependent CEC was arbitrarily established at pH 7.0 while the upper limit of the total pH-dependent CEC was considered to be at pH 8.0.

The KCl-exchangeable acidity, acidity extractable with a neutral N KCl solution, was subtracted from total acidity, acidity extracted with a $BaCl_2$-triethanolamine solution buffered

to pH 8.0, and the difference defined as pH-dependent acidity.

The conclusions which can be made with respect to the soils tested in this study can be summarized as follows:

1. It appears that Kansas soils do not exhibit such wide ranges of pH-dependent CEC values as reported by Pratt for California soils. The pH-dependent CEC of the Kansas soils tested ranged from 21.1 to 34.5% of the CEC measured at pH 8.0 while a range of from 28.1 to 74.6% was reported in the California soils. The low and narrow range of organic matter contents found in the Kansas soils was assumed to be the primary cause for the limited and narrow range of pH-dependent CEC values obtained.

2. The influence of pH upon the CEC of the Kansas soils was shown to result in a nearly linear increase in CEC between pH 2.5 and 6.0. On the average, CEC increased at the rates of 1.7, 2.1, and 3.8 meq/100 g per pH unit through the pH ranges of 2.5 to 6, 6 to 7, and 7 to 8, respectively.

3. It was concluded that the use of partial pH-dependent CEC alone was as adequate as partial pH-dependent CEC plus extractable aluminum for the estimating of lime requirement from regression equations. Furthermore, partial pH-dependent CEC was slightly better than either total pH-dependent CEC plus extractable aluminum for estimating lime requirement.

4. The use of multiple regression equations for estimating CEC using percentage clay and organic matter shows as much promise for use on Kansas soils as was reported for Wisconsin soils. This conclusion was based on multiple correlation coefficients (which ranged from R = 0.939 to 0.971) obtained between predicted and measured CEC at 6 pH levels.